CURE CYCLE DEVELOPMENT FOR HIGH PERFORMANCE COMPOSITES

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ABSTRACT

Hexcel Corporation's 8552 resin is a thermoplastic-toughened high-performance epoxy being used in the construction of advanced Army materiel. Understanding the cure behavior of a thermosetting system is essential in the development and optimization of composite fabrication processes. Torsional braid analysis (TBA) and differential scanning calorimetry (DSC) were used to establish a solid-state cure cycle for this epoxy system which will then be used to prepare composites for comparison to those prepared with the manufacturer's recommended cure cycle.

1. INTRODUCTION

Advanced Army composite structures are fabricated from a combination of thermosetting resin and fiber reinforcement. The thermosetting cure reactions are generally thermally induced, with high performance composites usually associated with high cure temperatures (200°C) to complete the cure. A manufacturer's recommended cure cycle, consisting of a series of temperature ramps and isothermal holds, is typically utilized for composite part fabrication. This entire cure cycle is carried out on a high temperature tool in an autoclave. Processing composite materials can be costly and time consuming. Solid state curing was sought to optimize the processing method (Breitigam et al., 1993). The goal of solid state curing of composites is to react a resin system in the tool at low temperature for as short of a time as possible, then complete the cure on a free standing part through a cure cycle in an oven. This would serve to: (1) Minimize tooling costs through the use of lower temperature materials; (2) lower capital equipment costs through more effective use of expensive equipment (i.e., autoclave); and (3) improve part quality through lower internal stress buildup through initial lower temperature cures

2. EXPERIMENTAL

TBA and DSC were used to develop a time-temperature-transformation (TTT) diagram for this development of a solid-state cure cycle. TBA has been utilized by others (Enns and Gillham, 1983; Gillham and Enns, 1994; Zukas, 1994) to establish isothermal TTT cure diagrams for thermosetting polymers. Its particular advantage is to graphically illustrate the different regions of a curing thermosetting system in terms of temperature and time. Knowing where these physical changes take place during the cure cycle of a composite component allows for better control of the fabrication process and ultimately better properties.

The composite material investigated in this study was a thermoplastic-toughened epoxy/graphite fiber system formulated by Hexcel Corporation, 8552-1. Samples of 8552-1 prepreg were received directly from Hexcel and stored at –20°C prior to analysis. DSC experiments consisted of subjecting a small amount of prepreg (10 to 20 mg) to a known thermal cycle and measuring the resulting exothermic heat of reaction of the sample. The heat of reaction obtained through DSC is directly proportional to the number of epoxy groups which have reacted and is thus proportional to the extent of reaction. TBA is a dynamic mechanical technique which measures the torsional rigidity and damping characteristics of a prepreg sample. TBA experiments were carried out on a fully automated system from Plastics Analysis Instruments, Princeton, NJ. Two primary thermal cycles were used in the TBA experiments: (1) isothermal cures (the sample was introduced into a preheated chamber) and (2) constant heat rate scans from room temperature to 275°C to determine the glass transition temperature (T_g) of an isothermally cured specimen, the degree of softening on heating, and the ultimate T_g of the fully cured prepreg.

3. RESULTS & DISCUSSION

Two maxima are typically observed in the damping response (log decrement) trace during an isothermal TBA experiment (the first thermal cycle described above). The first peak is typically associated with the process of chemical gelation. The mechanical response changes from a supported liquid to a solid. The second peak is typically associated with the process of vitrification. As a

sample cures to greater extents, the mechanical behavior changes from a rubbery response to a glassy one.

Gelation should occur at a constant extent of reaction. This onset of chemical crosslinking requires a particular extent of reaction, independent of cure temperature. Vitrification, however, should take place at higher extents of reaction as the cure temperature is increased. The process of isothermal vitrification indicates the glass transition temperature of the reacting resin is reaching the isothermal cure temperature. Higher extents of reaction are required to produce the higher glass transition temperature material reached with a higher isothermal cure temperature. Good correlation between the TBA results and the extent of reaction from the DSC results was observed in this study.

Free-standing cure during the oven cure cycle requires that the partially cured composite does not significantly soften and deform. This can be achieved through the proper selection of extent of reaction achieved in the initial cure and cure cycle parameters. The objective in cure cycle selection is to assure that the advancement of the glass transition temperature of the reactive resin proceeds at least at the same rate as extent of reaction. This will assure that the composite part will not soften as cure is completed.

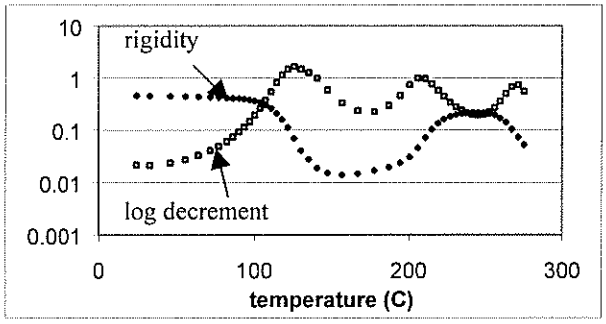

Figure 1. A 2.5°C/min TBA scan of 8552-1 prepreg cured 360 minutes at 120°C

Figure 1 illustrates the relative rigidity and log decrement traces of a 8552-1 prepreg sample isothermally cured at 120°C for 360 minutes then heated from room temperature to 275°C at 2.5°C/min. Three log decrement maxima are shown in this figure. First, a softening event takes place at about 125°C which represents the T_g of the material formed during the particular isothermal cure used. This event corresponds to a significant drop in rigidity. Second, a vitrification event takes place at about 210°C. Further cure during the thermal scan has raised the T_g of the curing resin higher than the physical temperature of the sample causing a return to the glassy state. Third, another softening event takes place at about 270°C which represents the fully cured T_g of the system. **Figure 2** illustrates the relative rigidity and log decrement traces of an identically cured 8552-1 prepreg sample as in **Figure 1,** except that it was scanned at 0.1°C/min. Very little softening of the sample is observed in the relative rigidity trace until the sample reaches its ultimate T_g. Complete cure was thus achieved with very little softening.

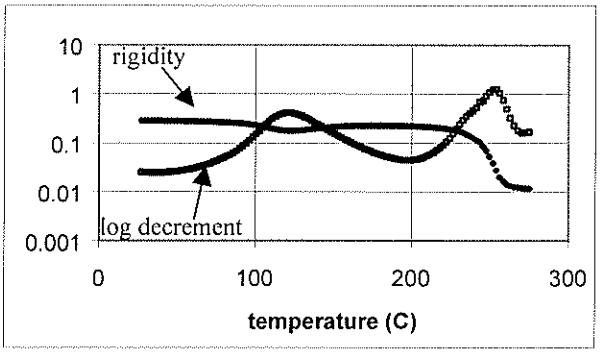

Figure 2. A 0.1°C/min TBA scan of 8552-1 prepreg cured 360 minutes at 120°C

SUMMARY

These figures represent only one cure condition. Extensive results were obtained for the 8552-1 system, investigating the variables of cure temperature, cure time, and scanning rates, and will be presented in greater detail. A TTT diagram was established and solid state cure cycles developed. Actual composite fabrication based on these cure cycles has been initiated.

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